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# Distinctive thermodynamic properties of solute-solvent hydrogen bonds in self-associated solvents

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## Abstract

Solute-solvent hydrogen bonding affects reactivity and other properties of dissolved species. In self-associated media, because of cooperativity and solvent reorganization, the thermodynamic functions of solute bonding with bulk solvent can be different from those of bimolecular solute-solvent complexes. Using available experimental data on the Gibbs free energies of solvation in aliphatic alcohols and water, we have determined the energies of solute-solvent hydrogen bonding for various proton accepting solutes. We show that the increase in the strength of hydrogen bonds because of the cooperative effect is strong for bonding with bulk water and significantly less so with bulk aliphatic alcohols. The hydrogen bonding Gibbs free energies for the same solute with bulk water and alcohol are correlated, but they correlate poorly with the energies of formation of the corresponding bimolecular solute-solvent complexes. Thus, the traditional hydrogen bond basicity scales, based on data for bimolecular complexes, do not correctly describe the thermodynamics of hydrogen bonding with self-associated solvents. Our results may help to define a separate solute basicity scale for associated media. Copyright © 2012 John Wiley & Sons, Ltd.

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## Keywords

cooperativity, Gibbs free energy, hydrogen bond, self-association, solute-solvent interactions, solvophobic effects